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INVESTIGATION OF THE FREE VOLUME CHANGES IN THERMALLY TREATED POLYETHYLENE BY POSITRON ANNIHILATION

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Positron lifetimes measurements in polyethylene were performed. Samples of the polyethylene were heated in the temperature range from 320 to 570 K. After cooling, the samples were used for the lifetime measurements in air at room temperature. A conventional fast-slow coincidence lifetime spectrometer was used for the measurements. Mean free volumes radii were calculated from the lifetime data.

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1. Introduction

Positron annihilation spectroscopy is widely used for investigations of different aspects of polymer properties [1, 2] and positron behaviour in polymers. The thermalised positron can annihilate with an electron from the absorber or it may form, with this electron, a bound system — positronium (Ps). The positron may form the Ps atom in amorphous regions of a polymer substance. In these regions, free volume exists where orthopositronium (*o*-Ps) may live for several ns. Polyethylene (PE) is one of the most common polymers. It is used all over the world for different purposes. It is also investigated by numerous authors [3–7]. The purpose of this paper was to investigate the influence of the annealing time and annealing temperatures on free volume in PE.

2. Experimental

A conventional slow-fast coincidence spectrometer with plastic scintillators was used. The time resolution of the spectrometer, approximated by two Gaussian curves, was determined by analysing the measurements of the positron lifetimes in kapton foils. Positron lifetime spectra were accumulated to approximately $(4.5\text{--}6.5) \times 10^6$ counts. The measurements were repeated at least twice for each sample. Parameters values obtained after numerical analyses of the raw lifetime spectra were reproducible. All of the measurements were performed in air at room temperature. All of the measured samples were made of PE produced by Instytut Chemii i Techniki Jądrowej, Warszawa (Poland), as thermo-shrunk sheets used

for electric cables insulation. Samples (9 mm in diameter) were cut down from a 1.3 mm thick sheet. The positron source, 0.2 MBq evaporated on kapton foil, was sandwiched between two pairs of such discs. The samples were annealed in two ways in an oven, in air, at different temperatures (from 320 to 570 K). The first set of the samples was annealed during 900 s at different temperatures. The second one was annealed at 473 K during different times (from 300 s to 14400 s). To evaluate the degree of the crystallinity and glass transition temperature values (T_g) of the investigated samples, differential scanning calorimetry (DSC) measurements were performed. A heating rate of 20°C/min was used during all of the measurements. There is no correlation between T_g and the condition of the annealing process. T_g changes from 253 K to 281 K for the both sets of the samples. The crystallinity, of the investigated samples, turned out to be constant: $(37 \pm 2)\%$.

3. Results

The positron lifetime spectra were analysed using the package programs PATFIT-88 [8]. These programs fitted four exponential components to the measured spectra. No constraints on lifetimes and intensities were imposed during numerical calculations. The longest-lived component, τ_4 , is attributed to the pick-off annihilation of *o*-Ps. According to a model proposed by Tao [9] and Eldrup et al. [10], the longest-lived component of the positron lifetime spectrum may be correlated with the mean radius of the free volume cavity in the polymer matter. They derived an equation

$$\tau_4 = 0.5 \{ 1 - R/(R + 0.1656) + (1/2\pi) \sin[2\pi R/(R + 0.1656)] \}^{-1}, \quad (1)$$

where τ_4 is the *o*-Ps lifetime expressed in nanoseconds, R is the mean radius of the spherical well expressed in nm, and 0.1656 nm is an empirical constant.

It seems that after a discussion between Yu et al. [11] and Jean [12] Eq. (1) may be still used to establish the relation between the τ_4 values and the mean radius of the spherical well. The aim of this investigation was to find out a relation between the annealing parameters of the thermo-shrunk PE and the mean radius of the free volume cavity. This is a reason why only τ_4 , I_4 , and R values (calculated according to Eq. (1)) are listed, as the results of this investigation, in Table I (for the annealed samples for 900 s, at different temperatures) and in Table II (for the annealed samples at 473 K for different times). Though the parameters of the annealing process were quite different it seems that the R values do not change remarkably. They are scattered about (0.332 ± 0.003) nm.

Equation (1) allowed to combine the mean radius of the spherical well with the concept of the specific or fractional free volume in polymers. This fractional free volume, denoted by f , is defined as

$$f = (V - V_0)/V = V_f/V, \quad (2)$$

where V is the total macroscopic volume of the polymer, V_0 is the volume occupied by molecules, V_f is the free volume of the polymer.

The fractional free volume might be determined from the lifetime measurements. The relative intensity of the *o*-Ps lifetime component, I_4 , is assumed to be proportional to the number of the free volume holes because it gives the information on the *o*-Ps formation probability. Wang et al. [13] and Kobayashi et al. [14]

TABLE I

τ_4 , I_4 , and R values obtained for the annealed samples (900 s) at different temperatures.

Annealing temperatures [K]	τ_4 [ps]	I_4 [%]	R [nm]
293	2574.2 ± 15.0	21.5 ± 0.4	0.333 ± 0.001
323	2584.1 ± 17.3	22.2 ± 0.4	0.333 ± 0.001
373	2566.9 ± 13.0	21.7 ± 0.3	0.332 ± 0.001
423	2546.6 ± 14.8	21.7 ± 0.3	0.330 ± 0.001
473	2556.1 ± 15.0	21.9 ± 0.4	0.331 ± 0.001
523	2544.3 ± 18.8	21.4 ± 0.5	0.330 ± 0.001
573	2596.7 ± 19.3	22.6 ± 0.5	0.334 ± 0.001

TABLE II

τ_4 , I_4 , and R values obtained for the annealed samples (473 K) at different annealing times.

Annealing time [s]	τ_4 [ps]	I_4 [%]	R [nm]
300	2650.8 ± 16.0	21.4 ± 0.4	0.338 ± 0.001
600	2600.5 ± 14.6	22.3 ± 0.2	0.334 ± 0.001
900	2556.1 ± 15.0	21.9 ± 0.4	0.331 ± 0.001
1200	2649.5 ± 16.9	22.2 ± 0.4	0.338 ± 0.001
1800	2610.8 ± 14.1	22.1 ± 0.3	0.335 ± 0.001
3600	2607.6 ± 14.1	22.2 ± 0.3	0.335 ± 0.001
7200	2604.6 ± 14.4	22.2 ± 0.3	0.335 ± 0.001
10800	2575.0 ± 12.7	21.7 ± 0.3	0.333 ± 0.001
14400	2551.5 ± 13.8	21.8 ± 0.3	0.331 ± 0.001

proposed a semiempirical relation which may be used to evaluate the fractional free volume f

$$f = AI_4V_{\text{sph}}, \quad (3)$$

where I_4 is the relative intensity of the *o*-Ps lifetime component, $V_{\text{sph}} = (4\pi R^3/3)$ [nm³] is free volume of the single hole (the R value is taken from Eq. (1)), A is the normalization constant.

The A value has not been measured in this work but as it is the constant, the f value must be proportional to the product: I_4V_{sph} . In Figs. 1 and 2 this product is shown either as the function of the annealing time or as the function of the annealing temperature. In the case of the annealing of the samples at 473 K, as the function of the time annealing (Fig. 1) it seems that the I_4V_{sph}

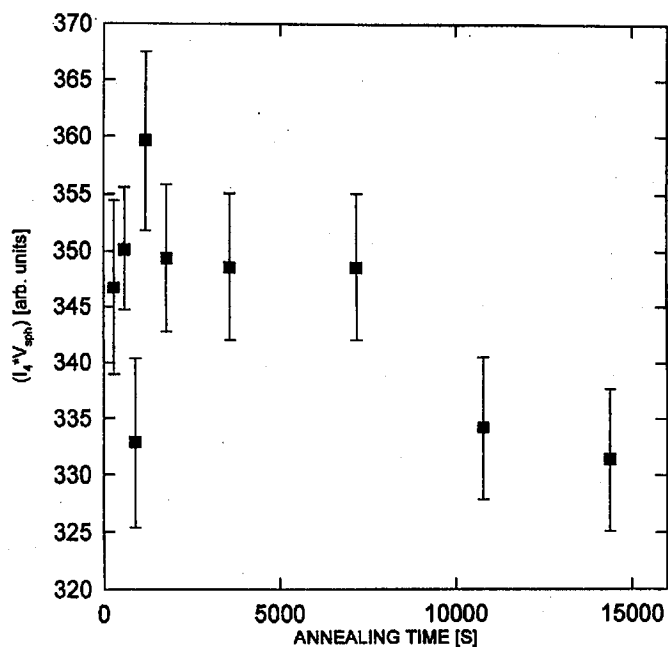


Fig. 1. The $I_4 V_{sph}$ values as the function of the annealing time at the constant temperature (473 K).

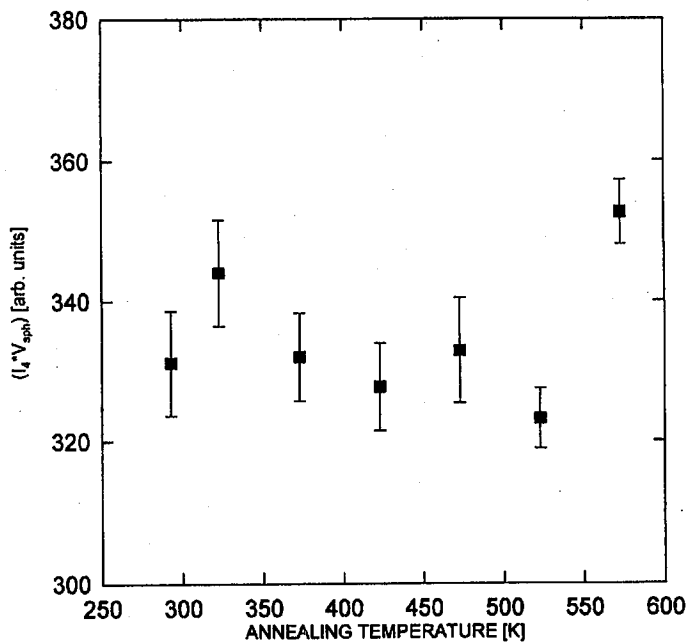


Fig. 2. The $I_4 V_{sph}$ values as the function of the annealing temperature at the constant time (900 s).

values decrease with the time of the annealing. For the annealing times from 300 s to 1200 s the experimental points are scattered roughly about $f = 350$. For the longer times of the annealing, these values slowly decrease. It seems to be obvious that these values are constant, as far as the different annealing temperatures are concerned (from room temperature to 570 K), Fig. 2. During the production process of the thermo-shrunk sheets, polymer chains are markedly stretched. Afterwards, during the annealing or heating of such sheets these chains shrink. It results in decreasing the fractional free volume, f , for the longer times of annealing, at 473 K. It suggests that the shrinking process of the PE chains is not already accomplished, for say four hours of the annealing, and the fractional free volume, f , still drops. Further investigations are needed to understand this phenomenon better.

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